Strongly Asymmetric Spectroscopy in Plasmon-Exciton Hybrid Systems due to Interference-Induced Energy Repartitioning

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Recent intense effort has been devoted to exploring different manifestations of resonant excitations of strongly coupled plasmons and excitons, but so far such studies have been limited to situations where the Fano- or Rabi-type spectra are largely symmetric at zero detuning. Using a newly developed full quantum mechanical model, here we reveal the existence of a highly asymmetric spectroscopic regime for both the Rabi splitting and transparency dip. The asymmetric nature is inherently tied to the non-negligible exciton absorbance and is caused by substantial interference-induced energy repartitioning of the resonance peaks. This theoretical framework can be exploited to reveal the quantum behaviors of the two excitation entities with varying mutual coupling strengths in both linear and nonlinear regimes. We also use prototypical systems of rhodamine molecules strongly coupled with AuAg alloyed nanoparticles and well-devised control experiments to demonstrate the validity and tunability of the energy repartitioning and correlated electronic state occupations, as captured by the variations in the asymmetric spectroscopy and corresponding nonlinear absorption coefficient as a function of the Au:Ag ratio. The present study helps to substantially enrich our microscopic understanding of strongly coupled plasmon-exciton systems.

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Plasmons describe the collective excitations of conduction electrons in metallic systems. Excitons describe individual electron-hole pairs in semiconducting or molecular systems. Recently, the interaction between plasmons and excitons in metal-semiconductor or metal-molecule hybrid systems has been actively investigated [1–7]. Such efforts may not only improve our understanding of the delicate nature of light-matter interaction via plasmon and exciton excitations [8,9] but also help to lay the foundation for developing novel sensing [10,11], photonic [12,13], and solar energy devices [14–17]. Therefore, a complete understanding and manipulation of plasmon-exciton coupling in physically realistic and technologically significant hybrid systems has been and remains an active subject of basic and applied researches in the field of nano- or quantum plasmonics [8,9,18,19].

In such hybrid systems, standing issues of timely importance include achieving tunability of the plasmon-exciton coupling strength, definitive experimental demonstrations of the strong coupling regime, and a full quantum mechanical description in diverse physical situations. In the strong coupling regime, the interaction of plasmons and excitons can be described by a new type of collective excitations called plexcitons [20–22], whose characteristics are dependent on the excitation strengths, damping rates, and spectral overlapping of the constituent counterparts [23–25]. Different manifestations of the plexciton resonances have been demonstrated in the line shape and energy splitting of the absorption spectra [26–46]. Various quantum mechanical model descriptions and physical realizations of both the transparency dip and Rabi splitting regimes have been carried out, with the common and distinct signature that the corresponding spectra are largely symmetric.

In this Letter, we develop a full quantum mechanical description of plexciton resonance by treating direct excitations of both plasmons and excitons on an equal footing. This highly desirable theoretical framework can be exploited to reveal the quantum behaviors and intrinsic relationship of the two excitation entities with varying mutual coupling strengths, including the extreme and technically more demanding cases of a single exciton and a single plasmon. Within this model, we first predict a novel and strongly asymmetric spectroscopic regime for both the Rabi splitting and transparency dip. The asymmetric nature is inherently tied to the direct and non-negligible absorbance of the excitons and is mechanistically caused by significant interference-induced energy repartitioning.
In the plasmon-exciton hybrid systems, the roles of plasmons and excitons are usually manifested by their distinctly different characters, i.e., the linewidth of the resonance and the coupling strength to the external field. In most hybrid systems, the linewidth $\Gamma_p$ and the coupling to external field $V_p$ of the plasmons are much larger than $\Gamma_c$ and $V_c$ of the excitons. Consequently, we can expect some typical absorption line shapes as shown in Fig. 1(a), where the asymmetric Fano resonance can be observed, when the energy detuning $\Delta = \omega_c - \omega_p$ between the resonant energies of plasmon $\omega_p$ and exciton $\omega_c$ is large. In this case, the plasmon resonance simply serves as an antenna to provide a continuous spectrum and mediates the coupling between the exciton and external field. On the other hand, when the detuning $\Delta = 0$, the absorption of the hybrid system is asymmetric as shown in Fig. 1(b), where the absorption spectra go through a transition from the typical Fano dip to the Rabi splitting resonances as we change the physical parameters of the system, e.g., the linewidth $\Gamma_p$ of the plasmon, to satisfy the criterion $V > (\Gamma_p - \Gamma_c)/4$ with $V$ indicating the internal plasmon-exciton coupling constant $[47]$. Essentially, with detuning $\Delta = 0$ and negligible coupling between one resonance (here, the exciton) and the external field, we should expect a symmetric absorption spectrum for the hybrid system with two coupled resonances.

In the present study, we go beyond the above prevailing picture by considering the more general case while the plasmons and excitons are both strongly coupled to the external field and develop a full quantum mechanical description with direct excitations of the plasmons and excitons treated on an equal footing. The absorption rate of the plexciton hybrid system is $\sigma_{\text{plex}}(\omega) = \sigma_{pp}(\omega) + \sigma_{cc}(\omega) + \sigma_{pc}(\omega)$, where

$$\sigma_{pp} = \text{Im}[n_p V_p^2 (\omega_n^c - \omega)/\sigma_0],$$
$$\sigma_{cc} = \text{Im}[n_c V_c^2 (\omega_n^c - \omega)/\sigma_0],$$
$$\sigma_{pc} = \text{Im}[2n_p n_c VV_p V_c/\sigma_0].$$

Here, $\sigma_{pp}$ and $\sigma_{cc}$ present the modified plasmonic and excitonic excitations, respectively, and $\sigma_{pc}$ is the crossing interference term; $\sigma_0 = (\omega_n^p - \omega) (\omega_n^c - \omega) - n_p n_c V^2$; $n_p$ and $n_c$ represent the population of plasmon and exciton modes, respectively; $\omega_j^p = \omega_j - i\Gamma_j/2$ ($j = p, c$) is the resonance energies; $V$ is the internal plasmon-exciton coupling constant. Those three terms corresponding to three different excitation and interference processes collectively can provide us much intriguing physical insight. Notice that the contribution of both $n_p$ and $n_c$ can be partially absorbed into the coupling strength and is independent of the incident power in the weak excitation regime. In the strong excitation regime, both $n_p$ and $n_c$ exhibit saturation behaviors of the quantum system $[49]$. For simplicity, we use $n_p = n_c = 1$ for calculations of the linear absorption spectrum.

Based on Eq. (1), we exhibit the absorption spectra of the hybrid system at detuning $\Delta = 0$ in Fig. 1(c), where the contribution of the different absorption terms has been presented separately. The first term $\sigma_{pp}$ provides a symmetric absorption feature, is similar to the result with $V_c = 0$ reported in Ref. [22], which represents the plasmonic excitation modified by excitonic transition, and can be obtained from bare plasmon resonance $\sigma_{p0} = \text{Im}[n_p V_p^2/(\omega_n^p - \omega)]$ by simply renormalizing the plasmon propagator with the plasmon-exciton coupling $V$. In this process, the molecules are not directly coupled to the external field, while the plasmon mediates a photon exchange between the molecules and external field. This term can also be viewed as the absorption of the hybrid system with the direct coupling between the molecules and...
external field $V_c = 0$ as shown in Fig. 1(a), where asymmetric Fano resonances at $\Delta \neq 0$ are also revealed.

The second term $\sigma_{cc}$ represents the excitonic excitation, now modified by the plasmonic transition. During this process, the exciton mediates the photon exchange between the plasmon and external field. Another way to understand this process is that the plasmon serves as a dissipation source, which strongly enhances nonradiative decay of the molecules, and thus significantly broadens the resonant peak of the excitons (see Fig. S1 in [48]). We note that the inequivalent role of the plasmon and exciton for $\sigma_{pp}$ and $\sigma_{cc}$ comes from their different intrinsic linewidths.

Most importantly, it is the very existence of the third term $\sigma_{pc}$ that leads to the prominent asymmetric spectral feature at the detuning $\Delta = 0$. This term describes the absorption through a delicate interference process. This interference induces repartitioning of the absorption spectra, by shifting the absorption spectral weight from high to low energy as shown in Fig. 1(c). In particular, this term, which is sensitive to all three coupling strengths ($V_p$, $V_c$, and $V$), can provide rich information about the hybrid system.

The repartitioning of the absorption spectral weight results in two remarkable features: (i) the largely asymmetric absorption strength of two split peaks at energy $\omega_-$ and $\omega_+$ labeled with intensity $\sigma_-$ and $\sigma_+$, respectively; (ii) the blueshifting of the absorption dip around $\omega_{dip}$ labeled with intensity $\sigma_{dip}$) from the exciton energy $\omega_c$. Both features can be clearly seen in Fig. 2, where the white dashed line tracks the energy of the absorption dip $\omega_{dip}$ and the blue solid lines track the energies of the absorption peaks $\omega_{\pm}$. From Figs. 2(a) and 2(c), we see that the spectra exhibit the typical Fano dip feature at small $V_c$. As $V_c$ increases, the spectra exhibit strong asymmetry, with $\omega_{dip}$ shifting away from $\omega_c$ and eventually approaching $\omega_+$, leading to the spectra with only one absorption peak. Conversely, when we fix $V_c$ and gradually turn on $V_p$ as shown in Figs. 2(b) and 2(d), the spectra gradually evolve from the one-peak-to-two-peak line shape. At small $V_p$, the spectra display one resonance peak from the exciton excitation, whose linewidth has been broadened due to its coupling to the plasmon. Consistent with the experimental result shown later, the strong asymmetric feature can be seen at large $V_p$ with two absorption peaks. In essence, we can also learn from the interference term $\sigma_{pc}$, to obtain such pronounced asymmetric spectra, both the plasmon and exciton should be strongly coupled to the external field.

The analytic expression of the shifting $\delta_d$ of the absorption dip from the resonant energy $\omega_c$ can also be derived theoretically. $\delta_d$ will be reduced to $n_cV_cV/V_p$ when $\Gamma_c \ll \Gamma_p$ and $\Delta \sim 0$; namely, the shift of the dip is proportional to the coupling between the plasmon and exciton. Another key point is that the electronic state occupations of the hybrids in the strong excitation regime are also treated when the power dependences of the populations $n_p$ and $n_c$ are taken into account. The analytic expression of the nonlinear absorption coefficient $\beta$ can be derived from Eq. (1). Here, we define $\beta(I) = [\alpha(I) - \alpha_0]/I$ with $\alpha_0$ standing for the constant linear part of the total absorption coefficient $\alpha(I)$. In the strong excitation regime, significantly enhanced saturation absorption (SA) ($\beta < 0$) and revised saturation absorption (RSA) ($\beta > 0$) are predicted at $\omega_-$ and $\omega_{dip}$, respectively. The enhanced SA at $\omega_-$ is caused by the energy repartitioning, while the RSA at $\omega_{dip}$ is induced by the coherent energy transfer from the plasmons to the excitons in the hybrids.

In the following, we provide control experiments to unambiguously verify the existence of the distinct asymmetric feature in the absorption spectra and the correlated electronic state occupations of the plexciton hybrids consisting of rhodamine molecules strongly coupled with AuAg alloyed nanoparticles. In these systems, we have large coupling $V_c$ and tunable other essential system parameters of $V_p$, $\Gamma_p$, and $n_p$. The nanoparticles were prepared by the sputtering technique. The damping rate, resonance intensity, and wavelength of the nanoparticle plasmon are tuned by the Ag ratio and particle size.

As shown in Fig. 3(a), the plasmon resonance peaks of all the different AuAg samples ($\rho_{Ag} = 0.78, 0.81, 0.85, 0.88, 0.91, 0.95,$ and 1.0) are successfully tuned to $550 \pm 5$ nm. As $\rho_{Ag}$ increases, the peak intensity of the plasmon resonance increases as well [Fig. 3(b)], which indicates that the density of states increases and the coupling strength $V_p$ effectively becomes stronger. Since the intrinsic linewidth of plasmon is significantly narrower.
in pure Ag than that in pure Au, a narrower intrinsic plasmon linewidth can be expected as $\rho_{Ag}$ increases. However, the inhomogeneous broadening due to size and shape distributions of the constituent nanoparticles becomes more significant as $\rho_{Ag}$ increases. These competing mechanisms give rise to the unusual $\rho_{Ag}$ dependence of the spectral width shown in Fig. 3(b).

The rhodamine B (RB) dye molecules with a strong absorption at 560 nm of the molecular exciton resonance were spin-coated onto the AuAg nanoparticles to obtain the RB@AuAg hybrids. The extinction spectra of RB@AuAg with different $\rho_{Ag}$ are presented in Fig. 4(a), which shows that the plexciton resonance is strongly dependent on $\rho_{Ag}$. When $0 \leq \rho_{Ag} \leq 0.78$, an asymmetric peak caused by the standard Fano interference is observed around 570 nm, where the strong absorption peak is induced by constructive interference of the two modes and, conversely, the absorption is suppressed by destructive interference on the high-energy side of this absorption peak. When $0.85 < \rho_{Ag} \leq 1.0$, two strong resonances $P_I$ and $P_{II}$ (with a maximum at $\lambda_- \rho$ and $\lambda_+ \rho$, respectively) are clearly demonstrated, which are induced by the coupling between the two modes. Additionally, the absorption minimum around $\lambda_{dip} = 515$ nm between $P_I$ and $P_{II}$ can be recognized as the Fano dip. In particular, we stress on the intriguing observation that the low-energy resonance $P_I$ is much stronger than the high-energy resonance $P_{II}$, due to the influence of $\rho_{Ag}$. When $\rho_{Ag}$ increases from 0.78 to 0.85 (which is the asymmetric Fano interference regime), the positions of $\lambda_+ \rho$ and $\lambda_- \rho$ slightly blueshift and redshift (less than 5 nm), respectively, and the corresponding strengths only slightly increase. When $\rho_{Ag}$ further increases from 0.85 to 1 (defining the Rabi splitting regime), $\lambda_+ \rho$ redshifts from 585 to 615 nm and $\lambda_- \rho$ blueshifts from 490 to 460 nm. Meanwhile, the resonant strengths of the two peaks significantly increase with $\rho_{Ag}$, but the increasing rate of the low-energy resonance $P_I$ is much faster than that of the high-energy resonance $P_{II}$, resulting in the distinct asymmetry as observed. The dip position ($\lambda_{dip}$) is almost independent of $\rho_{Ag}$, but the dip depth prominently increases with $\rho_{Ag}$.

Finally, the power-dependent absorption of the plexciton provides the information of occupations of the electronic states of the hybrids. The nonlinear absorption coefficient was measured by the Z-scan technique [50]. Figure 4(d) shows that the plexciton has SA and RSA at the wavelengths of $\lambda_+ \rho$ and $\lambda_{dip} \rho$. The SA effect of the RB@AuAg hybrids is much larger than that of bare AuAg nanoparticles. Specifically, $\beta(\lambda_+ \rho)$ significantly decreases from $-1.0$ to $-5.0$ cm/GW, while $\beta(\lambda_{dip} \rho)$ increases from $-1.0$ to $+3.8$ cm/GW as $\rho_{Ag}$ increases from 0.78 to 1.00. We stress that the observed $\rho_{Ag}$ dependencies of $\beta(\lambda_+ \rho)$ and $\beta(\lambda_{dip} \rho)$ can also be well explained by Eq. (1) with power-dependent populations at strong excitation. In particular, because $\sigma_{pc}$ is sensitive to changes in $n_p$ and $n_c$, it plays an important role in significantly modifying the nonlinear behavior. Collectively, these experimental observations convincingly demonstrate the existence of tunable repartitioning of the
absorption spectra and the unique correlated electronic state occupations of the plexciton systems.

In summary, using a combined theoretical and experimental study, we have established the existence of a highly asymmetric spectroscopic regime in plexciton systems, which is inherently tied to the direct and non-negligible exciton absorbance. The underlying mechanism is attributed to substantial interference-induced energy repartitioning of the plexciton resonance peaks. We have developed a full quantum mechanical description of the asymmetric spectroscopic regime with unusual power dependence and used prototypical systems of rhodamine molecules strongly coupled with AuAg alloyed nanoparticles to demonstrate the validity and tunability of the energy repartitioning and correlated electronic state occupations. The tunability has been achieved via varying the Au:Ag ratio. The asymmetric spectrum, revealing an inherent interference-induced energy repartitioning in strongly coupled systems, can be used as a powerful characteristic signature in future studies of such and related hybrid systems where the concept of the plexciton is valid. The present study helps to enrich our microscopic understanding of plasmon-exciton coupling and may find applications in quantum plasmonics and plasmon-based nanodevices.

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